Complexes of *Bis*(Dialkyldithiocarbamato)Arsenic(III) with Alkyldithiocarbonates: Synthesis and Characterization

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ABSTRACT

The reactions of $[R_2NCS_2]_2AsCl$ with KS_2COR' in 1:1 molar ratio at room temperature readily gave mixed derivatives of the type $[R_2NCS_2]_2AsS_2COR'$ [where, R = CH_3 and C_2H_5; R' = Et, Pr^n, Pr^i, Bu^n and Bu^i]. These derivatives are yellow crystalline solids. All these newly synthesized derivatives are soluble in common organic solvents like benzene, chloroform, carbondisulphide, acetone and dichloromethane etc. These derivatives have been characterized by melting points, elemental analysis (C, H, N, S and As) as well as spectral IR, NMR [^1H and ^{13}C] studies. On the basis of these studies tentative structures for these derivatives have been proposed.

Keywords: Arsenic; dialkyldithiocarbamate; alkyldithiocarbonate; IR spectra; ^1H and ^{13}C NMR spectra.

INTRODUCTION

The structural diversities in dialkyldithiocarbamates /1-17 /and alkyldithiocarbonates /15-23/ ligands is quite remarkable due to their bonding/coordination patterns with transition as well as main group metals /1-9,15-18/. Although a number of inorganic arsenic(III) dithiolates have been isolated and several of them characterized fully by single crystal x-ray analysis /1,5,12,15-19,21-23/ , relatively less attention has been paid to mixed 1,1-dithiolato ligands with arsenic(III) . In continuation of our interest in studies on group 15 elements with sulphur ligands /7-11,16,24-26/, we report herein some new mixed *bis*(dialkyldithiocarbamato)arsenic(III) complexes with alkyldithiocarbonates of the type $[R_2NCS_2]_2AsS_2COR'$ [where, R = CH_3 and C_2H_5; R' = Et, Pr^n, Pr^i, Bu^n and Bu^i].

EXPERIMENTAL

Materials and Methods

All the experiments were carried out under moisture free conditions. Solvents (benzene, alcohols, hexane, carbon disulphide, diethylether and dichloromethane etc.) were purified and dried by standard methods /27/. Sodium salt of dimethyldithiocarbamate (Fluka), sodium salt of diethyldithiocarbamate (BDH), arsenic trioxide (Merck) were used as received without further purification. Thionyl chloride (Merck) was distilled before use.

The alkyldithiocarbonates/28/, *tris*(dialkyldithiocarbamato)arsenic(III)/12/ and *bis*(dialkyldithiocarbamato)arsenic(III) chloride /12/ were prepared by reported methods. Arsenic trichloride was prepared by the reaction of arsenic trioxide and thionyl chloride /29/. Sulphur was determined gravimetrically as barium sulphate /30/. Arsenic was determined iodometrically /31/.

Melting points were determined on B10 Tech India Melting Apparatus and are uncorrected. Elemental analysis (C, H and N) was performed on a Heraeus Carlo Erba 1108 C, H, N analyzer. Infrared spectra were recorded on Perkin Elmer Model 557 as KBr disc in the range 4000 – 200 cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions on Bruker DRX300 (300 MHz FT NMR) spectrometers; chemical shift values ^{1}H and ^{13}C are expressed in δ ppm relative to TMS.

Preparation of *bis*(diethyldithiocarbamato)arsenic(III) isopropyldithiocarbonate

Equimolar amounts of *bis*(diethyldithiocarbamato)arsenic(III) chloride (1.10 g, 2.70 mmol) and potassium salt of isopropyldithiocarbonate (0.47 g, 2.70 mmol) in anhydrous benzene and carbondisulphide mixture (1:1) were stirred for ~ 4 hours at room temperature. Precipitated potassium chloride (0.19 g) was removed by filtration. Filtrate was concentrated to ~ 5 ml under reduced pressure. The yellow viscous liquid thus obtained was crystallized by adding 4-5 drops of anhydrous hexane and keeping it overnight in a refrigerator; the pale yellow solid thus obtained was dried on a vacuum pump. Yield – 1.08 g; 79%; M.P. 70°C (Table I). All the other derivatives were prepared by adopting the above methods. Pertinent analytical and physicochemical data for these complexes are listed in (Table I).

RESULTS AND DISCUSSION

Bis(dialkyldithiocarbamato)arsenic(III) alkyldithiocarbonate derivatives have been synthesised by reacting *bis*(dialkyldithiocarbamato)arsenic(III) chloride with potassium salts of alkyldithiocarbonate in equimolar ratios in anhydrous benzene and carbondisulphide (1:1) mixture by stirring at room temperature for ~ 4 hours.

$$[R_2NCS_2]_2AsCl + KS_2COR' \xrightarrow{\text{Benzene} + CS_2} [R_2NCS_2]_2AsS_2COR' + KCl\downarrow$$

(where, R = CH_3 and C_2H_5; R' = Et, Pr^n, Pr^i, Bu^n and Bu^i)

Table I

Physical and analytical data of *bis*(dialkyldithiocarbamato)arsenic(III) complexes with alkyldithiocarbonates

C No.	Compound	Yield (%)	KCl Found (Calc.)	M.P. ^{O}C	Colour & State	% Found (Calculated)				
						As	S	C	H	N
1.	$[(CH_3)_2NCS_2]_2AsS_2COCH_2CH_3$	82	0.12 g (0.12 g)	172	Pale yellow solid	17.43 (17.15)	43.98 (44.11)	24.59 (24.76)	3.66 (3.89)	6.61 (6.42)
2.	$[(CH_3)_2NCS_2]_2AsS_2COCH_2CH_2CH_3$	83	0.16 g (0.16 g)	160	Pale yellow solid	16.48 (16.62)	42.37 (42.76)	26.58 (26.66)	4.18 (4.22)	6.11 (6.22)
3.	$[(CH_3)_2NCS_2]_2AsS_2COCH(CH_3)_2$	88	0.15 g (0.15 g)	222	Pale yellow solid	16.68 (16.62)	42.56 (42.76)	26.50 (26.66)	4.11 (4.22)	6.07 (6.22)
4.	$[(CH_3)_2NCS_2]_2AsS_2COCH_2CH_2CH_2CH_3$	90	0.12 g (0.12 g)	195	Pale yellow solid	16.10 (16.12)	41.37 (41.45)	28.45 (28.43)	4.41 (4.52)	5.81 (6.03)
5.	$[(CH_3)_2NCS_2]_2AsS_2COCH_2CH(CH_3)_2$	89	0.13 g (0.13 g)	217	Pale yellow solid	16.07 (16.12)	41.32 (41.45)	28.41 (28.43)	4.37 (4.52)	5.89 (6.03)
6.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH_3$	88	0.21 g (0.21 g)	63	Pale yellow solid	15.23 (15.30)	38.95 (39.10)	31.49 (31.69)	4.98 (5.07)	5.52 (5.68)
7.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH_2CH_3$	91	0.19 g (0.20 g)	67	Pale yellow solid	14.57 (14.79)	37.98 (38.00)	33.15 (33.20)	5.45 (5.33)	5.61 (5.53)
8.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH(CH_3)_2$	79	0.19 g (0.20 g)	70	Pale yellow solid	14.64 (14.79)	37.88 (38.00)	33.10 (33.20)	5.20 (5.33)	5.58 (5.53)
9.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH_2CH_2CH_3$	84	0.23 g (0.24 g)	64	Pale yellow solid	14.24 (14.38)	35.82 (36.99)	34.53 (34.60)	5.62 (5.57)	5.30 (5.38)
10.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH(CH_3)_2$	87	0.21 g (0.22 g)	117	Pale yellow solid	14.34 (14.38)	36.78 (36.99)	34.56 (34.60)	5.28 (5.57)	5.13 (5.38)

All these newly synthesized derivatives are pale yellow solids. All these derivatives are soluble in common organic solvents like benzene, chloroform, carbondisulphide, acetone and dichloromethane, etc. The elemental analysis are also in accordance with their molecular formulae.

Infra-red Spectra

IR spectra of all these newly synthesised compounds have been recorded as KBr disc in the range 4000 – 200 cm^{-1} and tentative assignments of the important characteristic bands have been made with the help of earlier publications /7-11,24-26/.

The spectra of arsenic(III) dithiocarbonate derivatives exhibit very strong absorption bands in the regions 1225 – 1240 cm^{-1} and 1150 – 1170 cm^{-1} due to (C-O-C) and (C-O) stretching vibration, respectively. All these complexes show medium to strong intensity absorption bands in the region 1020 – 1040 cm^{-1} due to (C=S) stretching vibrations of both dialkyldithiocarbamate as well as alkyldithiocarbonate moieties indicating the bidentate nature of the both dialkyldithiocarbamate and alkyldithiocarbonate moieties with arsenic. All these derivatives also show medium to strong intensity absorption bands in the region 1425 – 1520 and 320-325 cm^{-1} due to (C=N) and (As-S) stretching vibrations, respectively.

^{1}H NMR

The ^{1}H NMR spectra of *bis*(dialkyldithiocarbamato)arsenic(III) complexes with alkyldithiocarbonates have been recorded in $CDCl_3$ solutions using TMS as an internal standard.

In the corresponding dimethyldithiocarbamate derivatives, the methyl protons appear as a singlet at 3.39-3.43 δppm thus suggesting the magnetic equivalence of these protons, while the diethyldithiocarbamate derivatives exhibit a triplet at 0.64-0.81 δppm and a quartet at 3.16-3.35 δppm due to CH_3 and CH_2 proton resonances, respectively (Table II).

In addition, these alkyldithiocarbonate derivatives also show expected proton resonances due to alkoxy protons of dithiocarbonate moieties /18-20/. The ethyl protons in ethyldithiocarbonate derivatives (Compound No.1 and 6; Table II) appear as a triplet and quartet at 1.40 δ ppm and 4.62 δ ppm due to CH_3 and OCH_2 proton resonances, respectively for the Compound No.1 (Table II), while for the Compound No.6 (Table II) the CH_3 protons of dithiocarbamate moieties and dithiocarbonate moieties are overlapping and exhibit a set of complex pattern signals in the range 0.64 – 0.78 δ ppm and a quartet at 4.16 δ ppm due to OCH_2 proton resonances. The n-propyldithiocarbonate derivatives (Compound No.2 and 7; Table II) appear as triplet at 0.74 – 0.96 δppm due to CH_3 protons, multiplet at 1.74-3.38 δppm due to middle CH_2 protons

Table II

^{1}H, ^{13}C and ^{31}P NMR spectral data (δppm) of *bis*(dialkyldithiocarbamato)arsenic(III) complexes with alkyldithiocarbonates

C.No.	Compound	H^1 NMR Chemical Shift (δppm)	^{13}C NMR Chemical Shift (δppm)
1.	$[(CH_3)_2NCS_2]_2AsS_2COCH_2CH_3$	1.40, t, 3H (CH_3 of xan) J = 6.00 Hz 3.43, s, 12H (CH_3 of dtc) 4.62, q, 2H (OCH_2 of xan) J = 6.00 Hz	0.93 (CH_3 of xan) 43.10 (CH_3 of dtc) 70.44 (OCH_2 of xan) 192.8 (NCS_2 of dtc) 216.1 (OCS_2 of xan)
2.	$[(CH_3)_2NCS_2]_2AsS_2COCH_2CH_2CH_3$	0.96, t, 3H (CH_3 of xan) J = 6.00 Hz 1.74-1.82,m,2H (CH_2 of xan) 3.42, s, 12H (CH_3 of dtc) 4.49, t, 2H (OCH_2 of xan) J = 6.00 Hz	10.37 (CH_3 of xan) 21.67 (CH_2 of xan) 43.14 (CH_3 of dtc) 74.9 (OCH_2 of xan) 192.8 (NCS_2 of dtc) 216.7 (OCS_2 of xan)
3.	$[(CH_3)_2NCS_2]_2AsS_2COCH(CH_3)_2$	1.34, d, 6H (CH_3 of xan) J = 6.00 Hz 3.39, s, 12H (CH_3 of dtc) 5.62, sep, 1H (OCH of xan) J = 6.00 Hz	0.8 (CH_3 of xan) 43.0 (CH_3 of dtc) 79.2 (OCH of xan) 198.2 (NCS_2 of dtc) 217.0 (OCS_2 of xan)
6.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH_3$	0.64-0.78, m, 15H (CH_3 of dtc and xan) 3.16, q, 8H (CH_2 of dtc) J = 6.00 Hz 4.16, q, 2H (OCH_2 of xan) J = 6.00 Hz	12.6 (CH_3 of dtc) 14.0 (CH_3 of xan) 48.2 (CH_2 of dtc) 78.8 (OCH_2 of xan) 198.8 (NCS_2 of dtc) 217.8 (OCS_2 of xan)
7.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH_2CH_3$	0.64, t, 12H (CH_3 of dtc) J = 6.0 Hz 0.74, t, 3H (CH_3 of xan) J = 7.0 Hz 3.35, q, 8H (CH_2 of dtc) J = 6.0 Hz 3.30-3.38,m, 2H (CH_2 of xan) 4.19, t, 2H (OCH_2 of xan) J = 7.0 Hz	10.49 (CH_3 of xan) 11.26(CH_3 of dtc) 20.39 (CH_2 of xan) 42.26 (CH_2 of dtc) 76.33 (OCH_2 of xan) 192.8 (NCS_2 of dtc) 216.0 (OCS_2 of xan)

8.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH(CH_3)_2$	0.81, t, 12H (CH_3 of dtc) J = 7.0 Hz 1.00, d, 6H (CH_3 of xan) J = 6.0 Hz 3.25, q, 8H (CH_2 of dtc) J = 7.0 Hz 5.58, sep, 1H (OCH of xan) J = 6.0 Hz	12.31(CH_3 of dtc) 13.68 (CH_3 of xan) 48.41(CH_2 of dtc) 78.6 (OCH of xan) 198.8 (NCS_2 of dtc) 217.8 (OCS_2 of xan)
9.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH_2CH_2CH_3$	0.68, t, 12H (CH_3 of dtc) J = 6.0 Hz 0.76, t, 6H (CH_3 of xan) J = 6.0 Hz 0.98-1.10, m, 2H (CH_2CH_3 of xan) 1.29-1.38, m, 2H (CH_2CH_2 of xan) 3.25, q, 8H (CH_2 of dtc) J = 6.0 Hz 4.32, t, 2H (OCH_2 of xan) J = 6.0 Hz	12.03(CH_3 of dtc) 14.1 (CH_3 of xan) 18.9 (CH_2 of xan) 41.0 (CH_2 of dtc) 46.7 (CH_2 of xan) 74.43 (OCH_2 of xan) 192.8 (NCS_2 of dtc) 217.3 (OCS_2 of xan)
10.	$[(C_2H_5)_2NCS_2]_2AsS_2COCH_2CH(CH_3)_2$	0.63-0.72, m (CH_3 of dtc + xan) 1.68-1.80, m, 1H (CH of xan) 3.26, q, 8H (CH_2 of dtc) J = 7.0 Hz 4.16, d, 2H (OCH_2 of xan) J = 6.0 Hz	11.8 (CH_3 of dtc) 14.1 (CH_3 of xan) 32.5 (CH of xan) 49.1 (CH_2 of dtc) 75.6 (OCH_2 of xan) 198.8 (NCS_2 of dtc) 216.2 (OCS_2 of xan)

s= singlet, d= doublet, t=triplet, q=quartet, m=multiplet, sep=septet

and a triplet at 4.19-4.49 δppm due to OCH_2 proton resonances, respectively. The i-propyldithiocarbonate derivatives (Compound No. 3 and 8; Table II) show doublet and septet in the region 1.00 – 1.34 and 5.58 – 5.62 δ ppm due to CH_3 and OCH proton resonances, respectively. The n-butyldithiocarbonate derivative (Compound No. 9; Table II) show triplet at 0.76 δppm due to CH_3 protons, multiplet in the region 0.98-1.10 δppm due to CH_2 attached to CH_3 protons, multiplet in the region 1.29-1.38 δppm due to CH_2 attached to OCH_2 protons and a triplet at 4.32 δppm due to OCH_2 proton resonances, respectively. The i-butyldithiocarbonate derivative (Compound No. 10; Table II) shows multiplet at 0.63 – 0.72 due to overlapping of CH_3 protons of dithiocarbamate and dithiocarbonate moieties as well as a multiplet and a doublet in the range 1.68 – 1.80 and 4.16 δ ppm due to middle CH and OCH_2 proton resonances, respectively.

^{13}C NMR

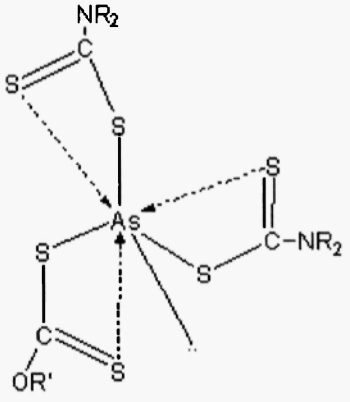
The proton decoupled ^{13}C NMR spectra (Table II) of these compounds have been recorded in $CDCl_3$ solutions using TMS as an internal standard. The ^{13}C NMR signals thus obtained are at reported values

without any appreciable shifts. The proton decoupled ^{13}C NMR spectra of the dimethyldithiocarbamate complexes show a signal in the region 43.0 – 43.14 δppm due to magnetic equivalent methyl carbon. The complexes of diethyldithiocarbamate show two signals, one at 11.26 – 12.6 δppm and the other at 41.0 – 49.1 δppm due to CH_3 and CH_2 carbons, respectively. All these compounds show a signal at 192.8 - 198.8 δppm due to NCS_2 carbon resonances of dialkyldithiocarbamate moieties.

In addition, these alkyldithiocarbonate derivatives also exhibit signals due to alkoxy carbons of dithiocarbonate moieties. The ethyldithiocarbonate derivatives (Compound No. 1 and 6; Table II) exhibit signals at 0.93 – 14.0 and 70.44 – 78.8 and δppm due to CH_3 and OCH_2 carbon resonance, respectively. The n-propyldithiocarbonate derivatives (Compound No. 2 and 7; Table II) exhibit signals at 10.37-10.49, 20.39-21.67 and 74.90-76.33 δppm due to CH_3, CH_2 and OCH_2 carbon resonances, respectively. The i-propyldithiocarbonate derivatives (Compound No. 3 and 8, Table II) exhibit signals at 0.80-13.68 and 78.6-79.2 δppm due to CH_3 and OCH carbon resonances, respectively. The n-butyldithiocarbonate derivatives (Compound No. 9, Table II) exhibit signals at 14.1,18.9,46.7 and 74.43 δppm due to CH_3, CH_2 (attached to CH_3), CH_2 (attached to OCH_2) and OCH_2 carbon resonances, respectively. The isobutyldithiocarbonate derivatives (Compound No. 10, Table II) exhibit signals at 11.8,14.1,32.5,49.1 and 75.6 δppm due to CH_3, CH and OCH_2 carbon resonances, respectively. All these compounds show signals of comparatively weak intensities in the region 216.0-217.8 δppm due to OCS_2 carbon resonances of alkyldithiocarbonate moieties.

STRUCTURAL ELUCIDATION

Although it is quite difficult to comment on the molecular structure of these complexes in solid state without actual X-ray crystal structure analysis of at least one of the products, however, two distinct signals in the region 1020 – 1040 cm^{-1} due to (C ⎓ S) stretching vibrations of dialkyldithiocarbamates as well as alkyldithiocarbonates in these *bis*(dialkyldithiocarbamato)arsenic(III) complexes with alkyldithiocarbonate derivatives indicate the weakly anisobidentate nature of both dithiocarbamate and dithiocarbonate ligands. On the basis of the above spectral data it may be concluded tentatively that these ligands behave as anisobidentate mode of attachment to the metal where one of the sulphur atoms is weakly coordinated, thus leading to a distorted octahedral geometry, with a stereochemically active lone pair of electrons.



Proposed Structure of the Complexes

where, X = COR' , R = CH_3 and C_2H_5, R'= Et, Pr^n, Pr^i, Bu^n and Bu^t.

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